A Theoretical Survey of Charged-Particle Recombination Processes in Gases

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Abstract

In this paper a survey is given of the theories applicable to the various recombination mechanisms. Both electron-ion and ion-ion recombination processes are dealt with. The theories involved, which are outlined only, are grouped into two parts, i.e., those applied at pressures below one atmosphere and those applied at higher pressures. The relation between the type of recombination process and the dependence of the recombination coefficient on the plasma parameters is discussed. The influence of the environmental conditions on the dominancy of a specific type of recombination process is illustrated. The correlation between experimental data and theoretical expectations is not emphasized.

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1. Introduction

Despite the considerable efforts that were made since 1897 in studying the recombination processes between ions, a thorough understanding of the mechanisms of all the processes involved is still far from being accomplished. In recent years attention has been drawn to this field due to the realization of the importance of recombination in limiting the ionization concentration which can be achieved in a large volume with a given ionizing source. This applies particularly to the ionized layers of the upper atmosphere--the ionosphere--which play an important part in radio propagation and more recently, the importance is magnified in relation to dealing with phenomena such as blackout and other space problems. Recombination is also dominant in gaseous discharges in containers at high pressures when losses by diffusion to the walls of the container are small. Recombination also plays an important part in determining the properties of the outer regions of the solar atmosphere, the solar corona in particular.

In this paper, an attempt will be made to present the theories dealing with the various processes of recombination. Recombination could be divided into two parts, according to the types of recombining charged particles, as follows:

a) Recombination of positive ions with electrons and

b) Recombination between positive and negative ions.

Since the gas pressure plays an important role in determining the dominant process of recombination, although the process itself might be independent of pressure within the range of consideration,

the various processes for each type of recombination could be grouped into two ranges namely, high pressure and low pressure recombination processes. High pressure will be defined as above-atmospheric pressure.

The recombination coefficient:

Consider an ionized region of a gas and assume that the region contains, at any instant, n^+ positive ions/cc and n^- negative ions/cc. If no source of ionization is present, then, due to recombination:

$$\frac{dn^+}{dt} = \frac{dn^-}{dt} = -\alpha n^+ n^- \tag{1}$$

i.e., the rate of change of ion density is proportional to the product $n^+ n^-$. The quantity α is known as the recombination coefficient which may depend on n^+, n^- or both. It could also be obtained in terms of the recombination cross-section $Q_r(v)$ from the following relation:

$$\alpha = \int_0^\infty v Q_r(v) \, f(v) dv$$

where $f(v)dv$ is the fraction of encounters between +ve and -ve ions in which the relative velocity lies between v and $(v + dv)$.

A solution of Eq. (1) can be obtained assuming the densities to be equal, i.e., $n^+ = n^- = n$. This gives:

$$n = \frac{n_o}{1 + n_o \alpha t}$$

where n_o is the density at the initial time $t = 0$.

A more applicable case to be considered is that in which ionization and recombination processes are proceeding simultaneously in a gas. This case is characteristic of the ionosphere and active plasmas. Assuming that ions are being produced at a constant rate of Q/unit volume/sec and that the only loss process is recombination, we have:

$$dn = (Q - an^2) \, dt$$

Let $Q/a = k^2$

$$n = k \frac{e^{2kat} - 1}{e^{2kat} + 1}$$

from which, the equilibrium concentration at $t = \infty$ is found to be:

$$n_\infty = k = (Q/a)^{1/2}$$

In general, it is recognized that all the ideal assumptions underlying the above treatments of recombination are not met in practice. Apart from the important effect of considering the case of anisotropy of ion production, i.e., when the produced ions do not possess an isotropic random distribution, investigations have indicated several factors which might have considerable influence on the recombination processes:

a) Multiple carriers of the same sign but of different a, with one carrier transferring to the other, are present during recombination.

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b) Inequality of densities of recombining carriers.

c) Impurities as low as 10^{-4}% have shown to be
important.

d) Higher modes of ambipolar diffusion.

Experimentally, one of the most successful techniques in the
study of recombination processes is the measurement of charged
particle densities in a disintegrating plasma usually referred to
as the afterglow. Earlier techniques used Langmuir probes for
measuring electron densities but a more successful method was
developed using microwave techniques.[1]

II. Low Pressure Recombination Processes

2.1 Electron-Ion Recombination Processes

a) Summary of Possible Reactions

Radiative recombination

It is a two-body recombination process by electron capture of
a positive ion into an excited atomic state. The excess electron
energy is given up as electromagnetic energy. The process is
therefore:

$$X^+ + e \longrightarrow X^* + h\nu$$

Dielectronic recombination

In a process of this kind, the surplus energy is taken up by
a second orbital electron in the positive ion so that a doubly
excited atom is initially formed. The doubly excited atom so
formed is energetically unstable, and if the excess energy is not
disposed of in some other way, it will revert back to the initial
condition releasing one electron and leaving the other in its
initial state; a process known as auto-ionization. There is a

finite probability, however, that alternatively, the doubly excited atom will undergo a radiative transition or a collision thereby dropping to a "stable" singly excited state.

The recombination sequence is therefore:

$$X^+ + e \longrightarrow X^{**}$$

$$X^{**} \longrightarrow X^* + h\nu$$

or
$$X^{**} + Y \longrightarrow X^* + Y + \text{kinetic energy}$$
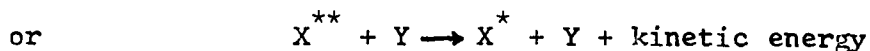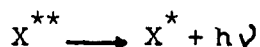
Dissociative recombination

If the positive ion is polyatomic, the surplus energy due to recombination may be transferred to energy of molecular vibration leading to dissociation of the molecule into fragments which may or may not be in their ground electronic states.

In the case of a diatomic molecule, we therefore have:

$$AB^+ + e \longrightarrow A^* + B^*$$

or

$$AB^+ + e \longrightarrow (AB)^* \longrightarrow A + B + h\nu$$
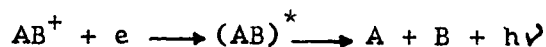
The case where both dissociated atoms may be in excited states is not energetically possible in the rare gases unless very high energy electrons are used, in which case the cross-section for recombination will drop to extremely low values. This is illustrated by the fact that the lowest possible excited states in rare gases are metastable states of energies close to the ionization energy of the diatomic molecule.

Taking helium as an example, we find that the first existing excited state is at an energy of 20 eV and since the ionization

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energy of $(He_2)^+$ is $\sim$ 23 eV, a 17 eV electron will have to be used in order to make the reaction possible energetically.

Three-body recombination

The excess energy can be taken up by a third body in the neighborhood of the interacting charges. The third body may be a neutral atom or molecule, a positive ion or an electron, the reactions being:

$$X^+ + e + Y \longrightarrow X + Y + \text{kinetic energy}$$

$$X^+ + e + e \longrightarrow X + e + \text{kinetic energy}$$
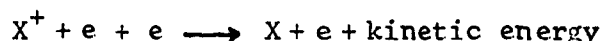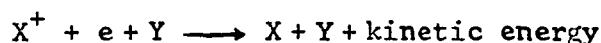
Wall recombination

This process is a special case of three-body recombination in which the walls of the container act as a third body in taking up the excess energy. Electrons and ions move towards the walls via ambipolar diffusion and recombination on the walls results from a relative two-dimensional motion of the ions on the wall surface. This process will be discussed in detail later.

The above processes summarize the possibilities of electron-ion recombination at low pressures. A detailed theoretical discussion of each process and the expected importance and magnitude of its recombination coefficient will now be presented.

b) The Radiative Recombination Process

It can be easily understood that the probability of radiative capture of an electron by an ion is quite small. Because measurements of lifetimes of excited atom states have shown that an electron must remain in the neighborhood of an ion for as long as 10^{-8} secs before there is a considerable chance of its

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undergoing a radiative collision.[2] If τ is the time of collision
in seconds, i.e., the time during which the impinging electron is
within the field of the ion, then the chance of emission of
radiation during the encounter is $10^8\tau$. τ is of the order of
10^{-15} secs for an electron of velocity 10^8 cm/sec ($\sim$ 3 eV). The
probability of capture to a particular level is, therefore, of
the order of 10^{-7}. Actually for capture by positive ions, there
are a number of accessible states into which capture may occur
and this increases the probability quite considerably. The long-
range Coulomb attraction also tends to maintain the incident
electron in the neighborhood of the ion, thereby further in-
creasing the probability of capture.

The cross-section for radiative capture may be calculated by
employing the quantum theory of radiative transition probabilities
which states that the transition probability is proportional to
the square of the amplitude of the electric dipole moment
averaged over the wave functions $\mathcal{Y}_i$, $\mathcal{Y}_f$ of the initial and
final state of the electron.

Hence, the transition probability $P_t = Ce^2 \left| \int\int \mathcal{Y}_i^* \, \vec{r} \, \mathcal{Y}_f \, d\tau \right|^2$
where $e\vec{r}$ is the electric dipole moment, r being the distance of
the electron from the centre of mass of the atomic (or molecular)
ion and C is the constant of proportionality. The cross section
is therefore obtained by appropriately normalizing the wave
functions and inserting the usual proportionality factor:

$$C = \frac{64\pi^4 \, \nu^3}{3hc^3}$$

where ν is the frequency of the emitted radiation.

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For radiative capture γ_f is a wave function for a bound state and is normalized so that:

$$\int \int |\gamma_f|^2 \, d\tau = 1$$

γ_i is the wave function for the initial "free" state normalized to have an assymptotic form of a plane wave of unit amplitude and the corresponding scattered wave (apart from the logarithmically varying phase factor due to the Coulomb field). If v is the initial velocity of the impinging electron, then the form of the initial wave function is given by:[2]

$$\gamma_i \sim v^{-1/2} \left[e^{ikz} + e^{ikr} \, r^{-1} f(\theta) \right]$$

where $k = \frac{mv}{\hbar}$ and m is the mass of the electron.

The cross-section for radiative capture of an electron from a free to the nth bound state can hence be written as:

$$Q_n(v) = \frac{64\pi^4 v^3 e^2}{3hc^3 v} \left| \int \gamma_i^* \, \vec{r} \, \gamma_{f_n} \, d\tau \right|^2 \qquad (1)$$

If the wave functions γ_i, γ_f are accurately known, Eq. (1) would correctly yield the cross-section for radiative capture, provided the wavelength of the emitted radiation is small in comparison with the dimensions of the atom in the state to which capture takes place, a condition satisfied in all cases of practical importance.

Examination of the dependence of the capture cross-section on the azimuthal quantum number "ℓ" may be done by employing

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spherical polar coordinates, following Morse and Stueckelberg,[3] and Wessel.[4] Typical results indicate that the largest contribution for a given principal quantum number n arises from values of $\ell \simeq$ n.

The most detailed calculations have been carried out by Bates,[5] et al., for the simplest recombination process of this kind, the radiative recombination of electrons with protons. They used a formula given by Oppenheimer[6] worked out in parabolic coordinates for the cross-section for capture to a state of given total quantum number n summed over all the substates of different azimuthal quantum number ℓ , giving:

$$\varphi_n = q_u{}^n + q_z{}^n$$

where:

$$q_u{}^n = A\,B \sum_{s=0}^{s=n-2} (s+1)(n-s-1) \left| F\left(1 - i\mu,\ 2 + s - n,\ 2,\ \frac{-4in\mu}{(n-i\mu)^2}\right) \right|^2$$

and

$$q_z{}^n = A\,C \sum_{s=0}^{s=n-1} \left| (n-s-1)\,F\left(-i\mu,\ 2+s-n,\ 1,\ \frac{-4in\mu}{(n-i\mu)^2}\right) \right.$$

$$\left. - (n-s-1) - \frac{2in\mu}{(n+i\mu)}\,F\left(-i\mu,\ 1+s-n,\ 1,\ \frac{-4in\mu}{(n-i\mu)^2}\right) \right|^2$$

$$A = \frac{8n^4\,\nu}{3\pi m^3 e^2 c^3}\ \operatorname{cosech}\ \pi\mu\ \exp\left[\pi\mu - 4\mu\ \arctan\ \frac{n}{\mu}\right]$$

$$B = \frac{32 \, n^2 \mu^{10}}{(n^2 + \mu^2)^4}$$

$$C = \frac{\mu^6}{(n^2 + \mu^2)^2}$$

$\mu = \dfrac{2\pi e^2}{h\nu}$ and $F(a, b, c, z)$ is the usual hypergeometric function.

Using these formulae, Bates, et al., evaluated Q_n for low electron energies for different values of n up to n = 40. This was rendered practicable by the use of the recurrence relation:[7]

$$(c-b)F(a,b-1,c,z) = b(1-z)\,F(a,b+1,\,c,z)$$
$$+ \left[(a-b)(1-z) + (c-b-a) \right] F(a,b,c,z)$$

To calculate the total radiative cross-section per ion for all possible radiative states "$q_r(v)$", it is therefore necessary to sum Q_n over all possible final states n to give:

$$q_r(v) = \sum_n Q_n$$

The calculations by Bates, et al., show that the series obtained is a slowly converging one so that in a recombination spectrum transitions from highly excited states should be quite strong. This result has been confirmed experimentally.

Further observations from the results of Bates, et al., indicate that the total recombination coefficient is quite small, as expected, even at the lowest electron energy utilized in the calculations although the rate of increase with decreasing electron energy is quite rapid.

The extrapolation of the results obtained for proton recombination to apply to recombination with heavier positive ions could be obtained rather easily unless very high accuracy is required.

The cross-section $Q_c(z,n,\ell,v)$ for capture of electrons of velocity v by a <u>bare</u> nucleus of charge ze into a state of quantum numbers n, ℓ is related to $Q_c(1,n,\ell,v)$ for capture into the corresponding state of a hydrogen atom by:[3]

$$Q_c(z,n,\ell,v) = z^2 Q_c(1,n,\ell,v) \qquad (2)$$

If the nucleus is partially screened by s bound electrons, the outermost occupied orbital having quantum numbers n_0, ℓ_0, the cross-section for capture into a level with quantum numbers n, ℓ, with $n > n_0$ could be obtained approximately by the same form of equation (2) provided a calculation is made to obtain the cross-section for capture into an orbital with quantum number n_0. The accuracy attainable in such calculations depends on the sensitivity of the integral of Eq. (1) to the detailed character of the wave functions. Bates[8] has shown that a good approximation is to use for the free wave function $\mathcal{Y}_i$, just that for motion in the field of a charge +e unmodified by the presence of the inner core, i.e., complete screening of orbital electrons. The most important result that could be obtained from Bates' calculations is that the cross-section for capture of an electron to the ground state of a heavy ion is of the same order of magnitude as that for capture by a proton.

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More sophisticated detailed calculations have been carried out for oxygen and neon by Seaton[9] using Hartree-Fock wave functions for the ground state of the atom and the "free" wave functions have been obtained by numerical integration of the wave function for the motion of the electron in the Hartree-Fock field of the ion. The conclusion that could be drawn from these calculations is that the contribution from the ground state to the total recombination coefficient is quite small indicating that no serious threat to the accuracy of the theory is possible unless a very large error in calculating this contribution is omitted which is extremely unlikely.

Some doubt was originally cast, however, on the validity of the theory from the observations of the continuous absorption coefficient of potassium made by Ditchburn, et al.[10] The observed coefficient was very low and exhibited a minimum at a wavelength of about 2700 Å. Early theoretical attempts to reproduce this behavior were unsuccessful, but a later investigation by Bates[11] revealed that, in this case, a very severe cancellation occurs in the integrand in the dipole matrix element so that extreme accuracy would be required in the wave function in order to give the correct cross-section. By introducing a variable polarization parameter to allow for the effect of polarization of the ionic core by the free electron, and calculating cross-sections for various values of this parameter, Bates was able to explain the observations quite well in terms of the theory.

Application of the preceding theory has been extended into the study of the four alkali metal atoms: sodium, potassium,

rubidium and cesium. The main observations by Ditchburn, et al.,[12] on sodium were reproduced by the theory using Hartree-Fock functions for both the initial and final wave functions. The definitely observed finite minimum in the variation with frequency of the absorption coefficient of rubidium and cesium[13,14] could be explained also by the theory, within the accuracy of the observations when allowance was made for spin-orbit coupling.

Experimental evidence in support of the calculated capture cross-section has been obtained by Mohler. He measured the intensity of the continuous spectrum radiated by the positive column of an arc discharge in cesium vapor and obtained therefrom an estimate of the cross-section for capture by Cs^+ of 0.3 eV electrons into the 6 p level of cesium. The method used was as follows:

The intensity $I(\nu)d\nu$ of radiation in a frequency interval between ν and $\nu + d\nu$ emitted by radiative capture to a particular level from a plasma containing N_e electrons and positive ions per cc is given by:[2]

$$I(\nu)d\nu = h\nu N_e^2 v Q_c(v) f(v)dv$$

where v is the velocity of an electron whose capture to the level considered gives rise to radiation of frequency ν so that:

$$h\nu = h\nu_o + \frac{1}{2} mv^2$$

Hence,

$$d\nu = \frac{mv}{h} dv$$

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where h ν_0 is the binding energy of the final state considered.

f(v)dv is the fraction of electrons with velocity between v $\&$ v + dv and $Q_c(v)$ is the cross-section for radiative capture of electrons having velocity v to the level in question (6 p level in this case). Assuming a Maxwellian distribution of velocities for the electrons in the positive column of an arc discharge and that the electron temperature is T_e, we have:

$$f(v) = 4\pi \left[\frac{m}{2\pi kT_e} \right]^{3/2} v^2 \exp \left[-mv^2/2kT_e \right]$$

Mohler measured $I(\nu)$, N_e, T_e therefore making it possible to obtain the cross-section for radiative capture $Q_c(v)$ provided the sources of radiation can be identified. Mohler investigated the intensity in the neighborhood of the 6 p limit and assumed that it was due to radiative capture to the 6 p level and applied various checks to varify his assumption. He found a value for the capture cross-section which agreed to within an order of magnitude with the theoretical calculations.

Radiative recombination plays an important role in many astronomical phenomena. It would be out of place in this review to attempt to describe all those phenomena in detail, but two examples will be briefly mentioned.

1) The theory of the solar corona:

It has been established that the kinetic temperature of this extreme outer region of the sun's atmosphere is very high, of the order of 10^6 °C. It is also important for many purposes

to obtain quantitative and qualitative information of the radiation emitted by the corona. For example, if the intensity of the coronal radiation in the high frequency region is far in excess of that expected from the usual model of the sun, namely, a black body at 6000°K, its influence on the production of ionization in the terrestial atmosphere might be quite profound. Woolley and Allen[15] made a starting attempt towards the theoretical investigation of coronal emission and show that the ionization equilibrium can be regarded as arising from a balance between ionization due to electron impact and radiative recombination, the contribution from photo-ionization being negligible. Proceeding in this manner, they were able to obtain data on the recombination coefficient assuming the kinetic temperature to be 10^{6}°C. It was found to approach unity when the energy required to further ionize an atom already in the sth state of ionization is about 400 eV. This was found to agree with spectroscopic data illustrating that the assumption of high kinetic temperature is consistent.

2) The study of the chemical composition of the intersteller gas:

Studies of this nature have been performed by Bates and Massey, Stromgen and Seaton. These workers have depended in their studies again on the equilibrium between atoms of an element in different stages of ionization. Under the stratified conditions which exist in interstellar space, it is evident that the important process in producing ionization is photo-ionization and not electron impact.

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c) Dielectronic Recombination

The possible importance of this process, which could be termed inverse auto-ionization was first suggested by Sayers[7] in 1939. A brief outline of the theoretical considerations of the process and a method for determining the recombination coefficient α as presented by Massey and Bates[16] will be given here.

The cross-section for capture of an electron into a doubly excited state of energy E_s above that of the ground state of the ion is given by:[17]

$$Q_c = w_s \; \frac{4\pi^2}{h v_s} \; \left| M \right|^2$$

where w_s is the statistical weight of the doubly excited state;

v_s is the velocity of the electrons of energy E_s;

$\left| M \right|$ is the transition matrix element of the interaction between the electron and the ion which makes the process possible.

Considering that the rate at which the doubly excited atom will decompose again into an ion and an electron "auto-ionization" is also proportional to $\left| M \right|^2$ with a lifetime θ given by:

$$\theta = \frac{h^4}{16\pi^3 w_2} \; \left[(2m)^3 \, E_s \right]^{-1/2} \Big/ \left| M \right|^2$$

where w_2 is the statistical weight of the ground state of the ion. Therefore,

$$\left| M \right|^2 = \frac{h^4}{16\pi^3 w_2} \; \left[(2m)^3 E_s \right]^{-1/2} \Big/ \theta$$

Substituting into the cross-section equation we obtain:

$$Q_c = \frac{w_s h^3}{w_2 4\pi v_s} (2m)^{-3/2} E_s^{-1/2} /\theta$$

If τ_s is the lifetime of the doubly excited state of the atom for stabilization in order that recombination be possible, then the cross-section for dielectronic recombination will be:

$$Q_d = \frac{\theta}{\theta + \tau_s} Q_c$$

Hence,

$$v_s Q_d = \frac{w_s h^3}{4\pi w_2} (2m)^{-3/2} E_s^{-1/2} /(\tau_s + \theta)$$

For all practical purposes, except when the gas pressure is very high, the stabilizing process of the doubly excited atom is one of radiation with τ_s of the order of 10^{-8} secs whereas θ is of the order of 10^{-13} secs and hence could be neglected.

Employing a Maxwellian distribution of velocities of the free electrons, the velocity values which contribute to the dielectronic process in this case, however, are discrete. Hence,

$$n(E_s) = \frac{2}{\pi^{1/2} kT} \left[\frac{E_s}{kT}\right]^{1/2} e^{-E_s/hT}$$

Therefore,

$$\alpha_s = \left[\frac{h^2}{2\pi mkT}\right]^{3/2} \frac{w_s}{2w_2} \tau_s^{-1} \exp\left[-E_s/kT\right] \tag{1}$$

Equation (1) gives the expression for the dielectronic recombination coefficient due to stabilization of the doubly excited atom from the sth state. To obtain the total recombination coefficient for all possible states, it is therefore necessary to sum

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over the available number of doubly excited states of the particular atom species in question.

Therefore,

$$\alpha_{Total} = \left[\frac{h^2}{2\pi mkT} \right]^{3/2} \sum_s \left[\frac{w_s}{2w_2} \right] \tau_s^{-1} \exp (-E_s/kT)$$

Since the statistical weights are usually of the order of unity, an important contribution can only arise from this process if E_s and kT are comparable in magnitude. Therefore, for atoms such as helium, for example, whose doubly excited states are of high energy, recombination of thermal electrons by the dielectronic process is quite small. Even for atoms such as neon and oxygen, a study of their energy levels yields a recombination coefficient of not greater than 10^{-12} cm^3/sec.

d)   The Dissociative Recombination Process

When Biondi and Brown applied the technique of measuring electron densities in a plasma using microwave energies to determine recombination coefficients in helium, argon, neon, hydrogen, nitrogen and oxygen,[1] the values obtained for recombination coefficients were in the range 10^{-8} to 10^{-6} cm^3/ion sec, approximately two orders of magnitude larger than those determined by Langmuir probe techniques. Further, the value consistently obtained for neon "2×10^{-7} cm^3/sec" is considerably greater than theoretically expected values (10^{-11} to $10^{-12} cm^3/sec$) for purely radiative recombination to the discrete atomic levels. Also, Biondi and Brown were unable to find spectroscopically any continuum of radiative energy characteristic of radiative recombination.
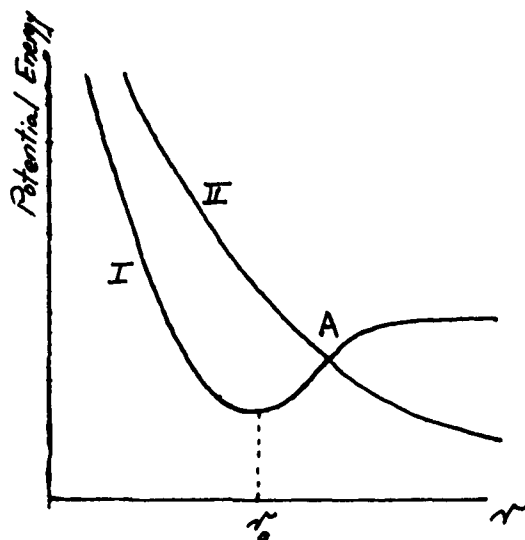
In order to explain these results in terms of a theoreti-
cal model, Bates[18] proposed that recombination took place between
the electron and a molecular positive ion, He_2^+, e.g., and named
the process dissociative recombination.

The nature of this process may be understood by referring
to molecular potential energy vs. nuclear separation curves.

Consider the potential energy curve for a diatomic molecule
shown in Fig. 1.

The following discussion will
follow very closely the excellent
explanation given by Massey for
illustrating the mechanism of dis-
sociative recombination.

Consider the potential energy
curves for the ground state of a
molecular ion $(AB)^+$, curve I in
Fig. 1, together with the potential
energy curves for different excited states of the neutral molecule
(AB) such as that for $(A' + B'')$(curve II). If the point of inter-
section of the two curves, point A, lies close to the equilibrium
internuclear distance of the diatomic ion $(AB)^+$, r_o, the dif-
ference in energy of the two systems AB^+ and $A' + B''$ could be
quite small. Therefore, at such an intersection, if the energy
balance is supplied to the diatomic ion AB^+ via an electron
having small kinetic energy, the system thereby formed will be in
energy resonance with the repulsive state of the neutral molecule
$(A' + B'')$. Hence, through a collision of a slow electron with the
ion AB^+ a transition may occur to this latter state leading to

two neutral and, in general, excited atoms A', B". It is, of course, self-evident that nuclear dissociation has to be affected before electron escape. Since the probability of this transition is obviously strongly dependent on the occurrence of the interaction near the equilibrium separation of the diatomic molecular ion, it is very difficult to estimate the actual rate of reaction for any particular ion.

Bates[18] was also able to demonstrate that the dissociative recombination coefficient could be several orders of magnitude larger than that for radiative processes. He argued that the process could be regarded similar to dielectronic recombination except for two differences which must be allowed for in the expression for the recombination coefficient obtained therein. The first difference is that the initial capture is not limited to a narrow electron energy range, as in the case of dielectronic recombination, by properly allowing for nuclear vibration. A factor $f(E)dE$ determined by the overlap of nuclear vibrational wave functions is introduced, normalized such that:

$$\int f(E) \ dE = 1$$

where the integration is performed over all possible vibrational transitions.

The second difference is attributed to the interpretation of τ_s. The neutral molecule formed by electron capture will be in a repulsive electronic state, thus, if the neutral system remains stable, the nuclei of the neutral diatomic molecule will separate. Once the separation becomes large, the probability of

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occurrence of auto-ionization to reverse the process will be small. The lifetime τ_s, in the dissociative recombination process, can be considered as the time taken for the nuclear separation of the neutral diatomic molecule to become large enough to insure the irreversibility of the dissociative recombination process and will be termed τ.

The expression for the recombination coefficient obtained assuming a Maxwellian electron velocity distribution about a temperature T, taking into consideration the effect of nuclear vibration is, therefore:

$$\alpha = \frac{w_1}{2w_2} \, h^3 (2\pi m\, kT)^{-3/2} \int \exp(-E/kT) \; f(E) \left[\theta(E) + \tau(E) \right]^{-1} dE$$

Substitution of the numerical values for the various constants gives:

$$\alpha = 2.1 \times 10^{-16} \, \frac{w_1 T^{-3/2}}{w_2(\bar{\theta} + \bar{\tau})} \int \exp(-E/kT) \; f(E) \; dE \quad cm^3/sec$$

where $\bar{\theta}$, $\bar{\tau}$ are average values;

    w_1 is the average integrated statistical weight of the excited electronic states of the neutral diatomic molecule possible as end products of dissociative recombination.

Taking: a) $\dfrac{w_1}{w_2} \sim 10$

      b) $\bar{\theta} \sim 10^{-13}$ secs; mean lifetime towards auto-ionization.

Since the velocity of nuclear separation[7] is of the order of 10^5 cm/sec and a change in separation of 10^{-8} cm is very likely to reduce the probability of auto-ionization to a negligible

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factor, $\overline{\tau}$ could be taken to be of the order of 10^{-13} secs. Hence,

c) $\tau \sim 10^{-13}$ secs.

If dissociative recombination takes place very close to the equilibrium nuclear separation f(E) will be large for small E since the vibrational energy will constitute a major proportion of the energy supplied by the electron to effect dissociative recombination. It can therefore be shown that the integral in this case will be of the order of kT. Hence,

d) $\int \exp\left(-E/kT\right) f(E) dE \sim kT$ for large f(E).

It is possible, therefore, to conclude that two ranges of electron temperature dependence exist, depending on the value of the integral. Contrary to the generally assumed variation of recombination coefficient with $T^{-3/2}$, a situation exists as in the case of a plasma afterglow, where only small deviations from the crossing point of the appropriate internuclear potential curves are implied. The temperature of the electrons is small and hence f(E) could be considered as constant over the range of electron energies yielding a recombination coefficient α which is proportional to $T^{-1/2}$. An exact analysis of the temperature dependence is very difficult, however, since the influence of the factor f(E) upon the over-all temperature variation of the recombination coefficient depends on a thorough knowledge of the pertinent molecular states.

Under the above assumptions, the value of the dissociative recombination coefficient at an electron temperature equal to room temperature is found to be of the order of 10^{-7} cm^3/ion sec.

This value is about five orders of magnitude larger than the value for the dielectronic recombination coefficient since stabilization by nuclear separation is about 10^5 times as rapid as stabilization by radiation.

This theory, therefore, also succeeds in explaining the experimentally observed high population of atomic states without recombination continua of emitted radiation.

Dissociative recombination was also found to be a dominant process in the ionosphere as concluded by Bates and Massey[19] from their study of ionospheric data.

Since dissociative recombination obviously depends on the density of molecular ions in a plasma a review of the experimental evidence and theoretical studies of the molecular ions in rare gases will be given. Spectroscopic investigation of He_2 by Weizel[20] established without question the existence of a stable molecular ion in helium. Molecular helium ions were also found through the use of mass-spectrometric techniques. Studies by Tuxen[21] in 1936 established the existence of molecular ions in the rare gases. The dissociation energies for such molecular ions are still subject, however, to some question. Several theoretical estimates have been made in order to determine the dissociation energy of He_2^+. For a detailed account of the different values obtained and their interpretations, the reader is referred to a survey of experimental work on electron-ion recombination by Anderson.[22]

After the discovery of band spectra in helium in 1913 by Goldstein and Curtis simultaneously, and the introduction of the

new field of quantum mechanics, the relation between the observed He$_2$ spectrum and quantum theory was reviewed by Weizel[20] in 1931. It is found that the He$_2$ molecule consists of an excited atom and a ground state atom in an attractive state and bound with about 2 eV.[22] The single excited electron moves in a molecular core $(1\ S\sigma)^2\ (2\ p\sigma)^2$, $1\Sigma_u$ which is the lowest electronic configuration of He$_2^+$. It is evident that the helium molecule dissociates via recombination into a ground state atom and a singlet or triplet excited atomic state.

Spectra emitted from rare gases other than helium at about 1 mm pressure do not show any molecular bands with two exceptions of weak band structures[23] found in a 50% mixture of helium and neon, and in a 50% mixture of argon and xenon[24] which probably are a result of dissociative recombination of the (NeHe)$^+$, and the (AXe)$^+$ molecular ions respectively.

The measured recombination coefficients were found to be larger in the heavier rare gases than in helium. This result is also consistent with the dominancy of the dissociative recombination process especially since atomic line radiation is an expected end result of such a recombination process and since diatomic ions are known to exist in the rare gases.

e) The Three-Body Recombination Process

In 1924, J. J. Thomson[25] successfully developed the theory for three-body recombination between ions. A review of this theory will be given in a later section when ion-ion recombination will be considered. In this section, however, we will adapt Thomson's theory to electron-ion three-body recombination.

For ion-ion recombination at low pressures in which the third body taking up the surplus energy is a neutral atom or molecule, Thomson gives the expression for the recombination coefficient as:

$$\alpha = \frac{2^{1/2}\,e^6}{81\,\varepsilon_o^3\,(\pi kT)^{5/2}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2} \left[\frac{1}{\ell_1} + \frac{1}{\ell_2} \right] \ m^3/sec \quad (1)$$

This expression holds for a gas with ions and electrons in equilibrium at a temperature T, i.e., in a disintegrating plasma (afterglow) where the electrons have cooled down to the gas temperature. (Approximately 50 μsecs after the ionizing energy has been removed.)

In Eq. (1):

M_1 and M_2 are the masses of the recombining ions;

ℓ_1 and ℓ_2 are the mean free paths for collisions between the respective ions and the gas atoms in which an amount of energy of the order of kT is transferred to a gas atom during such a collision;

T is the electron temperature.

It is noted that the expression for the recombination coefficient given by Eq. (1) shows a linear dependency of α on pressure. The recombination coefficient increases with increase in pressure up to pressures slightly below atmospheric where it becomes independent of pressure. The expression for α in the high pressure limit of the range under consideration is:[26]

$$\alpha = \frac{2^{1/2} \, e^4}{18 \, \varepsilon_o^2 \, (\pi kT)^{3/2}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2} \quad m^3/sec$$

It is also noted that the temperature dependence of α changes from $T^{-5/2}$ to $T^{-3/2}$ as the pressure increases.

The case of electron-ion three-body recombination can be deduced by allowing M_1 or M_2 to be very small. In this case, the only effective collisions leading to recombination are those in which the electron loses its energy to the third body, mainly the gas atom. The appropriate free paths for collisions of this type in an atomic gas, in which an amount of energy kT is transferred, will be of the order of $\frac{M \, \ell}{m}$ where

M is the mass of the gas atom,

m is the mass of the electron, and

ℓ is the mean free path for elastic electron colli-
    sions in the gas.

Hence, the recombination coefficient for electron-ion three-body interactions can be obtained from Eq. (1) by substituting

$\frac{1}{\ell_1} = 0$, i.e., the atoms are considered at rest,

$\ell_2 = \frac{M \, \ell}{m}$

$M_2 = m \ll M$

This gives

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$$\alpha \cong \left(\frac{8kT}{\pi\, m}\right)^{1/2} \frac{8\pi\, r_o^3 m}{3M\,\ell} \qquad (2)$$

where $r_o = \dfrac{2e^2}{3kT}$ is termed the critical distance and will be discussed in detail later.

Equation (2) yields the correct order of magnitude for the recombination coefficient for gas pressures up to the value that will make $r_o \cong \dfrac{M\,\ell}{m}$ after which Thomson's theory is not quite adequate. Also, Eq. (2) applies only to atomic gases.

It is possible to obtain a low pressure relationship between the three-body electron-ion recombination coefficient and its similar ion-ion recombination coefficient.[26] Assuming $M_1 = M_2 = M$ it is found that:

$$\alpha_{i-i} = \left(\frac{T_e}{T_i}\right)^{5/2} \frac{\ell_e}{\ell_i} \left(\frac{2M}{m}\right)^{1/2} \alpha_{e-i}$$

where:

> α_{i-i} is the ion-ion recombination coefficient, and

> α_{e-i} is the electron-ion recombination coefficient.

In a molecular gas, allowance must be made for the possible loss of energy by an electron to a gas molecule by exciting vibration, i.e., exciting inner molecular motion.[2] The fractional loss of energy "λ" by an electron in this type of interaction may be appreciably higher than $\dfrac{2m}{M}$. This would produce the effect of decreasing the mean free path "ℓ" by the same appreciable factor therefore resulting in an increase in the recombination coefficient. The expression for the recombination coefficient in a

molecular gas can therefore be deduced from Eq. (2) by re-placing $\frac{2m}{M}$ with λ .

At pressure ranges below 0.1 mm Hg approximately, it is ex-pected that three-body recombination becomes less effective, since this type of recombination depends by definition on the existence of a third body in the neighborhood of the colliding charged particles.

A possibility which has so far been ignored in this dis-cussion is the effect of neighboring charges on the rate of three-body recombination.

In a dense plasma (one in which the efficiency of ionization is very high) collisions in which two electrons and one ion are involved, could lead to three-body recombination since the transfer of excess energy could easily take place between the two electrons. This process is the inverse of highly excited atomic ionization by slow electron impact and in the afterglow such ion-ization and recombination processes could take place simultaneously.

The reaction is enhanced in rare gases where metastable states exist, producing high energy electrons via metastable-metastable interactions. The effective rate of recombination would depend, therefore, on the gradual change in the equilibrium between the capture and ionization processes. Estimates of the relative im-portance of these processes is rather difficult.

Owing to the long range of Coulomb interaction, the Thomson theory is not quite applicable, therefore, in this situation. It seems, however, probable that recombination via this process will decrease much more rapidly with increasing electron temperature

than with other recombination processes. This is due to the rapid decrease in the Coulomb scattering cross-section with relative velocity. In dense plasmas, at low electron temperatures, the importance of these effects would be demonstrated by a strong increase of the recombination coefficient value with increasing electron concentrations.

### f) The Wall Recombination Process

At low pressures, the order of one mm or less, in a dense plasma, electron diffusion becomes important. Electrons are able to diffuse out of the plasma towards the walls of the container, especially if electric fields exist to maintain a high electron energy level. Upon arriving they attach to the walls resulting in a build-up of negative potential relative to the plasma. This potential is called the "wall potential". This potential will facilitate a migration of positive ions to the walls and decreases the rate of electrons arriving. This continues until equilibrium is reached where the rates of electron and positive ion flow are equal. This process, known as ambipolar diffusion, permits the attainment of a neutral plasma while a constant removal of ions and electrons is taking place. This process if further facilitated by the fact that electrons and positive ions, upon arrival at the wall, eventually neutralize each other. Neutralization occurs via an interesting process called "wall recombination".

Since diffusion of electrons and ions along the wall lies in a two-dimensional plane, this limitation on the degrees of freedom of random motion could actually speed up the diffusive approach phase of the recombination process. However, nothing is known

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regarding the speed of diffusion along surfaces except that it might be large on glass surfaces.[27] When the ion and electron enter their attractive force region, the probability of the "encounter" leading to capture and recombination is almost unity. This follows, since the surface is always present as a third body for absorbing the excess energy. It is concluded that the wall recombination process is rapid enough so as to have no effect on the ambipolar diffusion. The time rate of charge loss "recombination" is therefore controlled by the ambipolar diffusion to the walls. The latter, being a slower process, will insure that the disappearance of the ions from the plasma will follow the exponential law of decay characteristic of ambipolar diffusion. Therefore, it would be quite difficult to properly evaluate a wall recombination coefficient from the exponential decay curve.

2.2 Ion-Ion Low Pressure Recombination Theory

Plasmas generated in electron-attaching gases contain both positive and negative ions as well as electrons. The negative ions are formed in the plasma by direct attachment of electrons, in addition to charge transfer and exchange processes. At first glance, one might disregard rare gases in the discussion of ion-ion recombination. However, recent experimental evidence[26,28] showed that helium could stably attach an electron to form a negative ion with a probable configuration $1s2s2p, {}^4P_{5/2}$ and its presence could be of importance since its detachment requires only 0.075 eV and could therefore be responsible for the reaction:

$$He^- + X + 0.075 \text{ eV} \longrightarrow e + He(2^3s) + X$$

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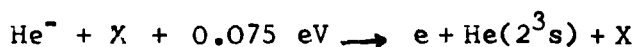
In electron attaching gases, however, one can summarize the possible mechanisms for positive ion-negative ion recombination, at below atmospheric pressures, into the following:[2]

a) Radiative Recombination: $X^+ + Y^- \longrightarrow XY + h\nu$

b) Mutual Neutralization by Charge Exchange: $X^+ + Y^- \longrightarrow X^* + Y^*$

c) Three-body Recombination: $X^+ + Y^- + Z \longrightarrow XY + Z$

Since the first two are two-body processes, they are likely to be important only at low pressures below 1 mm Hg. Three-body recombination however becomes important at pressures above a few mm Hg.

a) The Radiative Recombination Process

This type of process is essentially a radiative transition between two excited electronic states of the formed molecules XY. The initial excited state must be one which dissociates into the positive and negative atomic ions X^+ and Y^- at infinite nuclear separation.

The probability per collision may be estimated in a similar manner to that for electron radiative capture by a positive ion discussed in Chapter II.

It is found that the recombination coefficient at room temperature of the gas is unlikely to be larger than 10^{-14} $cm^3/$ ion sec.

b) The Mutual Neutralization Process

From gas-kinetic considerations, it has been found that the effective collision cross-section between two atoms in which electron transitions occur is very small unless the change of internal energy ΔE is very small, and that for comparable transitions, the variation of cross-section with ΔE generally follows a

resonance curve. The manner in which the cross-section varies with ΔE can also be explained by the gradual character of the collisions since the atoms approach each other with a very small velocity compared with that of the orbital electrons (neglecting Coulomb forces for the moment). The orbital electrons will therefore have ample time to readjust themselves to the slowly varying condition without necessitating a transition; this will result in the impact being very nearly adiabatic. This problem may be represented classically by considering the case of applying a time dependent disturbing force to an oscillator of natural frequency ν and studying its effect. It is immediately evident that the effect would be strong if the collision time τ is small with respect to the natural period of the oscillator. Applying this to the collision problem, since τ is of the order of a/v where a is the interaction range between the atoms and v is their relative velocity, the condition for weak excitation becomes:

$$a\nu/v \gg 1$$

The quantum mechanical condition is obtained by replacing:

$$\nu = \Delta E/h$$

where ΔE is the internal energy change involved in the transition. Therefore, the probability of occurrence of a transition during impact will be small if:

$$a\Delta E/hv \gg 1$$

The case of exact resonance is therefore that in which $\Delta E = 0$.

Consider now the case of transfer collisions in which the resonance is imperfect, i.e., $\Delta E \neq 0$ but has a finite small value. ΔE is termed the resonance defect. Mutual neutralization is essentially a charge exchange process in which the electron may be captured into any state of the neutral atom X thereby leaving a neutral atom Y in another state provided energy is conserved. The probability will be, however, a strong function of the final states of X, Y and will exhibit a maximum value at a particular pair of finite states.

Bates and Massey[29] have estimated the recombination coefficient for such a process by applying the theory of crossing of potential energy curves[2] which stems from the above basic discussion. In the case of ions, however, due to the Coulomb interaction, the velocity of approach is thereby increased with a subsequent exceptionally large increase in the range of the interaction energy V_i between the initial pair of colliding systems. The crossing point at which $V_i - V_f = \Delta E$, the resonance defect will be given approximately by:

$$R = - e^2/\Delta E \qquad (1)$$

where V_i and V_f are the initial and final interaction potential energies, including the internal energy of excitation. R is the separation between the two nuclei of the colliding ions.

For the case of a superelastic collision in which there is a net gain in the energy of the relative motion due to the impact, ΔE is negative; therefore a real crossing point always exists for any superelastic collision.

When ΔE is positive, no real crossing point exists. There is, however, a finite probability for the colliding system to jump into the final state when it is supplied by ΔE through kinetic energy.

In the case of mutual neutralization:

$$\Delta E = A - I + E_x + E_y$$

where: A is the electron affinity of the atom of species Y;

I is the ionization energy of the atom of species X;

E_x, E_y are the excitation energies of the respective atoms in their final states.

Bates and Massey have used this approach to study in detail the mutual neutralization process in oxygen. For a summary of this work, the reader is referred to reference 2 of this paper. They found that the recombination coefficient for mutual neutralization of O^+ and O^- ions was unlikely to be much larger than 5×10^{-8} cm^3/ion sec and that the range lay between 5×10^{-8} and 5×10^{-9} cm^3/ion sec. They also found that in the temperature range from 250° to 1000°K the recombination coefficient was approximately proportional to $v^{-1/2}$.

c)   The Three-Body Recombination Process

After the establishment of the theory of three-body recombination by J. J. Thomson in 1924, Jaffe' in 1940, 1941 subjected the general problem of the recombination process to an extensive study using a broad statistical approach. His conclusions showed that the Thomson theory, as well as Langevin and Harper's theories for higher pressures, were but special limited cases

which apply only where the specialized ideal conditions justifying the use of these relationships as such. He showed that recombination processes generally depended on the relative values of three basic parameters:

a) r_o, the average separation in distance between carriers of opposite sign.

b) λ, the mean free path of the carriers.

c) d_o, the radius of a sphere of active attraction. In Thomson's theory, d_o represents "the distance from one ion at which the energy of thermal agitation of the ion of opposite charge, just equals the potential energy of the ion pair.

The three parameters r_o, λ, d_o are determined by:

1) The nature of the ions;

2) The nature of ionizing processes;

3) The efficiency of ionization;

4) The anisotropies of ion production;

5) The ambient gas temperature;

6) The ambient gas pressure.

The Thomson theory in principle involves four basic periods or steps that the ions go through until the recombination process is completed.

These four periods may be covered in detail during a recombination process, as in the case of recombination of positive and negative ions in air and similar gases below one atmosphere at relatively low ion densities. However, for other recombination processes, one or more of these steps may be absent or modified. Thomson depended in his analysis on the three critical parameters,

r_o, λ, d_o indicated by Jaffe'. The four steps are the following:

    a) The Diffusive Approach Period.

    b) The period of Active Attraction (within the sphere of attraction).

    c) The period of Orbital Encounter.

    d) The period of Charge Transfer.

The Diffusive Approach Period

The carriers of opposite charge being at a large distance initially "r" such that the Coulomb potential energy e^2/r is small compared to their random thermal energy $3/2\ kT$, will diffuse quite at random. This random motion through diffusion will continue until two ions of opposite charge arrive to within a distance d_0 of each other.

The period of Active Attraction

If the distance d_o between the positive and negative ions is taken such that: $\dfrac{e^2}{d_o} = \dfrac{3}{2}\ kT$ or $d_o = \dfrac{2}{3}\ \dfrac{e^2}{kT}$ then the volume within a sphere of radius d_o, called the sphere of active attraction,[27] will define a region throughout which the Coulomb forces between the ions will be of such a magnitude so as to change the random diffusion drift to a directed motion pulling the ions towards each other.

The nature of the motion within d_o, however, is determined by the mean free path magnitude "λ" relative to d_o. If $d_o \gg \lambda$, many collisions will be encountered by the ions as they approach each other and their relative velocity will be determined by

their mobilities, i.e., $v = (\mu_+ + \mu_-) \dfrac{e^2}{r^2}$ since $v = \mu E$. If

$d_0 \simeq \lambda$, then no collisions occur and the ions will move

solely under the influence of Coulomb attraction forces and will

therefore have higher relative velocities reducing the probabil-

ity of recombination. This explains the small probabilities of

three-body recombination at low pressures.

The period of Orbital Encounter

Depending on whether energy is removed from one of the ions

or not, i.e., $d_0 \gg \lambda$ or $\lambda \gg d_0$ respectively, the path of

the ions about their common centre of mass will either be an

open hyperbolic one in which case the ions will separate beyond

d_0 and charge transfer may not be accomplished, or, when $d_0 \gg \lambda$

the orbit becomes an elliptical path until the next encounter

for either ion at which the energy changes and brings the ions

closer together, or knocks them apart so that they execute

hyperbolic motions again and escape beyond d_0.

The period of Charge Neutralization

This period is quite similar to the case of mutual neutral-

ization and the same theoretical discussion could be applied

taking into account that the slight excess energy after neutral-

ization could be taken up as kinetic energy of the two now

neutralized atoms.

Thomson, using the above reasoning, applied the conditions in

order to obtain an expression for the three-body recombination

coefficient in terms of the masses of the recombining ions, as-

suming Maxwellian velocity distributions and that an energy loss

by either ion of kT due to collision with the third body in the

sphere of active attraction was sufficient to ensure closed

elliptical orbit encounter and subsequent recombination. He
obtained, for low pressures, i.e., $d_0 < \lambda$

$$\alpha = \frac{64}{81} (2\pi)^{1/2} \frac{e^6}{(kT)^{5/2}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2} \left[\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right]$$

where M_1, λ_1 are the mass and mean free path of one recombining
ion.   ion.

M_2, λ_2 are the mass and mean free path of the second
recombining ion.

For high pressures in which $\lambda < d_0$, the recombination
coefficient should reach a constant saturation value given by:

$$\alpha = \frac{16}{9} (2\pi)^{1/2} \frac{e^4}{(kT)^{3/2}} \left[\frac{M_1 + M_2}{M_1 M_2} \right]^{1/2} \tag{2}$$

It will be seen later that the Thomson theory is not quite
accurate at high pressures and therefore the expression for α
given by Eq. (2) is only correct around atmospheric pressures.

For details of the development of the expressions for the
three-body recombination coefficient, the reader is referred to
the original paper by Thomson.[25]

III. High Pressure Recombination Processes

It is expected that, in gases at above atmospheric pressures,
the recombination mechanisms would proceed in a different manner
than those in the cases when the pressure is low. It will be
shown that the proper recombination mechanism would proceed in
agreement with one of two theories by Langevin and Harper which
are quite closely related. The application of either theory will

be shown to be dependent only on the pressure of the gas under study.

At high pressures, it is important to realize the influence of the production mechanism on the observed recombination. Since the recombination process is unique, the influence of ion production will be interpreted in this paper in terms of observation phenomena.

Langevin Theory of Recombination at High Pressures

In 1903, Langevin[30] derived an expression for the ion-ion recombination coefficient. He considered the gas to be sufficiently dense so as to simulate to the ions immersed in it a continuous resisting medium. He also assumed the positive and negative ions to drift towards each other under the influence of their mutual Coulomb forces. (Note the difference between Langevin's theory and Thomson's theory where the latter assumes a diffusive approach period.)

The assumption of a high density medium allowed Langevin to determine the relative velocity of the colliding ions via mobility considerations.

He obtained an expression for the recombination coefficient as:

$$\alpha = 4\pi e(\mu_+ + \mu_-)$$

where μ_+, μ_- are the mobilities of the positive and negative ions respectively. This theory was at first accepted without question to give the correct theoretical value of α for all ion-ion recombination. The expression for the recombination coefficient shows that it should vary inversely as the pressure, i.e., α

proportional to $1/p$, since the mobility of an ion is inversely proportional to its ambient gas pressure. This was found to be not true at below atmospheric pressures since the observed data indicated that the recombination coefficient decreased with decrease in pressure below one atmosphere. This now can be explained since Langevin theory applies strictly so long as there is no diffusive approach, i.e., so long as both recombining ions lie originally within d_o; a situation which does not necessarily exist at lower pressures.

The Langevin-Harper Process

This type of recombination is again described by the three critical parameters r_o, d_o, λ. Volume recombination at high pressures, in which isotropic and random ion distribution is assumed corresponds to the conditions $r_o > d_o$, $d_o > \lambda$. It is seen that this set of conditions emphasizes the diffusive phase (this is the source of error in Langevin's theory at about atmospheric pressures) and allows the recombination process to be virtually completed once the ions enter the sphere of active attraction by free diffusion.

Harper[31] in 1932, made a careful analysis of Langevin's theory for high pressure three-body recombination. He concluded that diffusion must predominate over drift due to Coulomb attractive forces at slightly above atmospheric pressures and proceeded to obtain an expression for the recombination coefficient under these conditions. He used, for the velocity of radial motion, an expression given by:

$$\frac{dr}{dt} = \frac{3(D_+ + D_-)}{r} \qquad (1)$$

where D_+ and D_- are the diffusion constants of the positive and negative ions respectively.

Harper obtained on this basis an expression for the recombination coefficient under the assumption that a third body is always available within a sphere of radius d_0 to take up the excess energy. This expression is given as:

$$\alpha = 4\pi \, d_0 3(D_+ + D_-) \tag{2}$$

Taking $d_0 = \dfrac{e^2}{3kT}$ gives the radius of the sphere of active attraction obtained by Harper on the basis of a balance between the velocity due to Coulomb attraction forces and that due to diffusion. (This is identical to the value of d_0 used by Thomson.) Substituting the value of d_0 in Eq. (2) gives:

$$\alpha = 4\pi \, \frac{e^2}{kT} \, (D_+ + D_-)$$

From Einstein's relation:

$$\frac{\mu_+ + \mu_-}{D_+ + D_-} = \frac{e}{kT}$$

Hence, assuming a Maxwellian distribution, $T_+ = T_- = T$

$$\alpha = 4\pi e(\mu_+ + \mu_-)$$

where μ_+, μ_- are the mobilities of the positive and negative ions respectively.

It is noticed that Harper's recombination coefficient is identical to the expression for the recombination coefficient

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obtained by Langevin's theory. This striking result was dis-
cussed by Jaffe'[32,33] where he presented a more detailed analysis
and found the recombination coefficient to be:

$$\alpha = 4\pi d_o f_1 (D_+ + D_-)$$

where f_1 is a constant resulting from averaging processes which
is close to unity.

The value for the radius of the active sphere of attraction
"d_o" however, was more rigorously given by Jaffe' as:

$$d_o = \frac{e^2}{K\ kT}$$

where K is the dielectric constant of the medium. Jaffe'
pointed out that the Langevin and Harper processes are in prin-
ciple different, though they lead to approximately the same
relation via $\alpha_{Harper} = f_1\ \alpha_{Langevin}$.

This explained why Langevin's theory was experimentally
found to hold for pressures above two atmospheres in air while,
under the conditions given by Langevin ($d_o \gg r_o$, $d_o \gg \lambda$) it
should hold at pressures around 100 atmospheres.

It is believed that the weak point in this discussion lies
in the uncertainty when dealing with Brownian motion in mutual
force fields where both positive and negative ions are acted on
by additional random forces.

The Langevin-Harper recombination coefficient is seen to be
proportional to the ion mobilities, varies inversely as the gas
density, and is relatively insensitive to temperature changes at
constant densities.

3.1 High Pressure Electron-Ion Recombination

At high pressures, the average distance between carriers, "r_o" becomes small and the mean free path for electrons "λ" will consequently decrease. Thus it is possible for the radius of the sphere of active attraction d_o, as defined in the previous section, to be larger than either r_o or λ.

In this case, it might be expected that an electron removed from an atom would lose its energy within the distance d_o and since it will be continually under the influence of the Coulomb forces due to its parent positive ion, the diffusive approach period would not exist and the electron will most likely recombine with its parent ion. Recombination under the above conditions, viz., $d_o \gg r_o \gg \lambda$ is referred to as a Preferential Recombination Phenomenon.

The phenomenon of preferential recombination was discussed from a general theoretical point of view by N. E. Bradbury.[34] He came to the conclusion that for electron-ion recombination this phenomenon is not likely to be encountered experimentally. This could be explained from the argument that, in a nonelectron-attaching gas which is pure at high pressures, electrons will usually escape from the region of active attraction before losing their energy and be captured.

Some attempts were made to try to observe this phenomenon through cosmic-ray studies in chambers filled with inert gas at very high pressure ($\sim$ 10 atmospheres), and measuring ion currents as a function of sweep fields. The results obtained, however, were shown to be caused by improperly designed sweep fields and

not, therefore, indicative of any such type of influence on the recombination process. Thus, it seems at this time that preferential electron-ion recombination is a possible but apparently not observed phenomenon.

3.2 High Pressure Ion-Ion Recombination

Various influences of the production mechanism on the recombination between positive and negative ions have been established. They are:

a) Preferential Recombination Phenomenon

As defined in Sec. 3.2, this influence is likely to occur when $d_o \gg r_o$, $d_o \gg \lambda$.

Preferential ion-ion recombination was independently discovered and named by workers studying cosmic rays in high pressure chambers.[27] They found that very high fields were required to draw out all the ions produced by cosmic radiation and obtain saturation currents. This was attributed to the anisotropy of the ion production mechanism. Therefore, those high fields are necessary to counteract the Coulomb attraction forces and separate the ions. A very general outline of the theory of such production influence was proposed by Bradbury,[34] as mentioned previously, which requires a set of assumptions regarding electron attachment.

The role of ion-ion preferential recombination is important, even in inert nonelectron-attaching gases, since it is quite impossible to obtain adequate purity control due to the contribution of negative ion forming impurities from the walls at high pressures. It can be concluded that at very high pressures recombination does not exist throughout the volume, all recombination being preferential.

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b) Columnar Recombination Phenomenon

It was observed by Bragg and Kleeman[35] while studying the
ionization in gases produced by α particles that saturation
currents were harder to obtain with α-particle ionization than
with other methods of ionization. Moreover, they observed that
saturation was most difficult when the particle paths were paral-
lel to a uniform electric field rather than normal to it.
Moulin[36] showed that the phenomena was attributed to the non-
uniform distribution of ions along the ionizing path of the α
particle. Jaffe'[37] came to the same conclusion from his studies
on ionization in liquids and developed the first part of his
theory of columnar ionization and recombination.

Let us examine the ionization of an α particle as it moves
along a certain path. It is expected that intense initial ion-
ization will be produced very close to the trajectory of the
α particle. It is produced by the action of the Coulomb forces
of the energetic α particle on the outer electrons of the neigh-
boring atoms, hence, the intensity of ionization (density of ions
produced) will decrease rapidly away from the trajectory.

The ejected electrons, possessing a large energy, will
therefore diffuse outward and after a certain period of time
(around 10^{-3} secs) most of them will probably attach to molecules
forming negative ions. In actuality, however, due to the nonuni-
form radial density distribution the electrons will not diffuse
freely and due to the large charge density, ambipolar diffusion
might allow for outward motion of the positive ions also.

Jaffe' in developing the theory has made the following
assumptions:

a)   After a certain period of time ($\sim 10^{-4}$ secs) the positive and negative ions are symmetrically distributed radially about the axis of the α particle trajectory.

b)   The density of positive and negative ions decreases radially outward following a Gaussian distribution curve.

c)   Recombination and diffusion are both taken into account since they are continuously existing at all times considered.

d)   Recombination does not change the form of the Gaussian distribution of density.

e)   At t = 0, $n = \dfrac{N_o}{\pi b^2} \, e^{-r^2/b^2}$

    where

n = concentration of ions as a function of distance "r" from the axis at a time t = 0

b = a constant related to the average displacement r_o of the Gaussian curve from the column axis $r_o = b(\pi/4)^{1/2}$.

f)   When t is very large, the column approaches a nearly random distribution.

    Jaffe' obtained the expression for the concentration of the ions as a function of the distance r from the axis and time t as:

$$n = \dfrac{N_o}{1 + \dfrac{\alpha N_o}{8\pi D} \ln \left(\dfrac{4Dt + b^2}{b^2} \right)} \; \dfrac{e^{-\dfrac{r^2}{(4Dt + b^2)}}}{\pi(4Dt + b^2)}$$

where D is the diffusion coefficient of the ions and α is the true recombination coefficient which should naturally be independent of the production mechanism.

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Jaffe' has also been able to determine the fraction of ions that have escaped from the column and columnar recombination, he gives the "escape fraction" as:

$$\frac{N_1}{N_o} = -\int_{\zeta_0}^{0} \frac{e^{-\zeta} \, d\zeta}{1 + \frac{\alpha N_o}{8\pi D} \log \frac{\zeta_0}{\zeta}}$$

where
$$\zeta_0 = R^2/b^2$$
$$\zeta = R^2/(4Dt + b^2)$$

R is the radius of a coaxial cylindrical surface such that every ion at a distance $r > R$ is said to have escaped. R could be determined by the separation between two columns in the gas (or liquid).

We now return to the problem of variation of the magnitude of "saturation" currents, obtained from a particle ionization in an electric field, with the angle the a particle makes with the field. Jaffe' has studied the problem and obtained the following:

For the general case of an electric field of strength X, making an angle ϕ with the a particle trajectory, the ratio of the escaping ions N_∞ to those initially generated N_o, is given by:

$$\left(\frac{N_\infty}{N_o} \right)_X = \frac{1}{1 + \frac{\alpha N_o}{8\pi D} \sqrt{\frac{\pi}{z}} \, S(z)}$$

where:

$$z = \frac{b^2 \mu^2 x^2}{2D^2} \sin^2 \phi, \quad \mu = \text{ion mobility}$$

$$S(z) = \frac{1}{\sqrt{\pi}} \int_{0}^{\infty} \frac{e^{-s}ds}{s(1 + \frac{s}{z})}$$

This equation applies only when X and ϕ are not too small. This theory has been verified by the experimental data obtained by Moulin and has proven to be extremely successful.

c)   Initial Recombination Phenomenon

G. Rumelin, in his studies of gamma-ray ionization observed an apparent initial fast decrease in the value of the recombination coefficient measured over very short periods of time. This decrease continued over varied periods of time following ionization after which it reached the known constant value. S. G. Plimpton observed the same phenomena in X-ray ionization and gave the interpretation as follows:

Since the initial distribution of negative and positive ions is non-isotropic, relative to each other, then the negative ions formed by electron attachment might be distributed such that they lie in pairs near their recombining positive ions. Therefore, if their average separation is r_i where $r_o > r_i > d_o$ and $d_o > \lambda$ recombination will occur more rapidly. This could be expressed by an effective concentration n′ which will be a function of r_i as compared to the relation between the concentration n and r_o. As time proceeds, however, the ions will diffuse towards a more random distribution and n′ approaches n. Therefore, the rate of decay of charged particle density will decrease with time towards the constant value of true three-body volume recombination.

It is possible therefore to conclude that initial recombination responsible for apparent high values of a initially is caused by an initial nonuniform ion distribution in pairs, which, by diffusion becomes more uniform and accounts for the apparent decrease in the recombination coefficient with time so that the real value is finally approached.

An exact evaluation of this phenomenon theoretically is quite difficult. Bradbury[34] outlined the general theory involving initial recombination and Loeb[27] obtained an approximate solution for the case of air. The results depicted by Loeb and by Bradbury[34] agreed quite well with experimental evidence obtained by Gardner,[38] Sayers,[39] Marshall[40] and others. It was observed that the apparent decrease in a was either hyperbolic or exponential. Loeb[27] in his analysis shows the exponential dependence of the rate of disappearance of ions on time.

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